Theoret. chim. Acta (Berl.) 27, 325—338 (1972)

CNDO/2 Calculations and Configuration Analyses for Some Hydrogen-Bonded Systems

H. Morita and S. Nagakura

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato, Tokyo, Japan

Received August 14, 1972

The potential energy curves of hydrogen-bonded systems were calculated for the water, methanol, and formic acid dimers and for the hydrogen maleate ion by a modified CNDO/2 method, the core resonance integrals between σ-electrons being distinguished from those between π-electrons, the different bonding parameters being used for –O– and =O, and the core potential integrals V_{AB}^c for O–H, C=O, and O···O being determined semi-empirically. Consequently, the following results were obtained: 1) a potential energy curve with a single minimum at $r(\text{O–H}) = 0.95$ Å and with a concavity near 1.70 Å for the linear chain dimers of water and methanol; 2) a symmetrical potential energy curve with two minima at $r(\text{O–H}) = 0.95$ and 1.78 Å for the cyclic dimer of formic acid; 3) a flat-bottomed symmetrical potential energy curve for the hydrogen maleate ion. The configuration analysis method was applied to the hydrogen-bonded systems; the contributions of the covalent ($(\text{O–H–O})^{-1}$) and ionic ($\text{O}^-\text{H}^+\text{O}^-$) structures being 54% and 39%, respectively, for the symmetrical hydrogen bonding of the hydrogen maleate ion.

Die Kurven potentieller Energie von Systemen mit H-Brücken wurden im Fall von H_2O-, CH_3OH- und HCOOH-Dimeren und für das Hydrogen-Maleatanion mittels eines modifizierten CNDO-Verfahrens berechnet, wo für Rumpf-σ- und -π-Elektronen jeweils verschiedene Resonanzintegrale und verschiedene Bindungsparameter für =O und –O– verwendet und wo die Rumpfpotential-Integrale für O–H, C=O und O···O semiempirisch bestimmt werden.
Die Resultate sind 1) eine Potentialkurve mit einem einfachen Minimum für lineare Ketten von H_2O und CH_3OH, 2) eine symmetrische Potentialkurve mit zwei Minima für das cyclische Dimere von HCOOH und 3) eine Potentialkurve mit einem flachen Minimum für das Maleatanion. Konfigurationsanalyse ergab einen Beitrag von 39% für die ionischen Strukturen.

1. Introduction

The potential energy curves of hydrogen-bonded systems are important to understand their physico-chemical and biological properties. From the theoretical point of view, the determination of their potential energy curves has hitherto been performed by many authors semi-empirically [1–5] and non-empirically [6, 7] for the water, alcohol, and formic acid dimers, and also for the guanine-cytosine and adenine-thymine base pairs. On the other hand, the experimental determination of the potential energy curves has scarcely been made. In a previous paper [8], we determined the double minimum potential energy curves for the formic acid and acetic acid dimers from the analysis of their overtone bands which appear in $5000 \sim 12000\ \text{cm}^{-1}$.

For the purpose to compare the experimentally determined potential energy curve with the theoretical one, we have undertaken to study the electronic structure of the hydrogen-bonded formic acid dimer by a semi-empirical method in which the CNDO/2 method [9–13] is modified by taking bonding parameters consistent with the core resonance integrals used in the Pariser-Parr-Pople method [14, 15] for π-electron systems and semi-empirically determined core potential integrals. The same theoretical method has been extensively applied to the hydrogen-bonded water and methanol dimers, and also to the hydrogen maleate ion. The structures of hydrogen-bonded alcohols have been discussed by several authors from the experimental view-point [16–20], but, concerning them, there are still problems to be solved. The hydrogen maleate ion is an interesting research subject, because its hydrogen bond is extraordinary strong as revealed from its short oxygen-oxygen distance of 2.437 Å and may be expected to have the large covalent character.

Baba, Suzuki, and Takemura [21] presented the configuration analysis method in which the wave functions of such substituted aromatic hydrocarbons as aniline, phenol, and aminonaphthol are expanded with regard to ground, locally(within a parent hydrocarbon and a substituent group)-excited, and charge-transfer (between a parent hydrocarbon and a substituent group) configurations. This method was found to be useful for understanding the natures of the ground and excited states of the substituted aromatic hydrocarbons. We have undertaken to apply this method to inter- and intra-molecular hydrogen-bonding systems, expecting that vivid interpretation can be obtained for the natures of hydrogen bonds, in particular for their covalent or charge-transfer characters.

2. Methods of Calculation

Modified CNDO/2 Method. The calculation procedure is essentially the same as the original CNDO/2 method presented by Pople, Santry, and Segal [9, 10], but some modifications have been made concerning the evaluation of two-center integrals, bonding parameters, and core potential integrals.

(a) The one-center Coulomb integrals γ_{AA} concerning the valence electron orbitals of the hydrogen, carbon, and oxygen atoms are taken to be 12.845, 11.144, and 13.707 eV, respectively [11].

The two-center Coulomb integral γ_{AB} between the two valence ($2s$ or $2p$) orbitals on the A and B atoms was determined by Klopman's semi-empirical equation [11], γ_{AB} between σ and π electrons being taken to be equal:

$$\gamma_{AB}=e^2\Bigg/\left[R_{AB}^2+\frac{1}{4}\left(\frac{e^2}{\gamma_{AA}}+\frac{e^2}{\gamma_{BB}}\right)^2\right]^{\frac{1}{2}}, \tag{1}$$

where R_{AB} is the distance between the A and B atoms.

(b) The core resonance integrals β_{pq} between σ electron orbitals were distinguished from those between π electron orbitals by the equation presented by Bene and Jaffé [12].

Furthermore, the oxygen atoms of the carbonyl and hydroxyl groups were treated differently from each other, by adopting different bonding parameters, $\beta^0(=\text{O})=-26.5$ eV and $\beta^0(\text{–O–})=-50.3$ eV. The bonding parameters for the hydrogen and carbon atoms, $\beta^0(\text{H})$ and $\beta^0(\text{C})$, are taken to be equal to -12.0 and -16.7 eV, respectively. These bonding parameters were determined in such a way that the calculated β_{pq} between π orbitals coincides with the core resonance integral used in the Pariser-Parr-Pople method [14, 15].

(c) The core potential integral, V^c_{AB}, necessary for the calculation of the total energy was represented by the following equation in the present study:

$$V^c_{AB} = Z_B \gamma^c_{AB} = Z_B \left[\gamma_{AB} + c \left(\frac{e^2}{R_{AB}} - \gamma_{AB} \right) \right]. \tag{2}$$

Here, Z_B is the core nuclear charge of atom B, and a parameter, c, was determined for each valence bond in such a way that the calculated equilibrium bond length coincides with the observed one. The ordinary CNDO/2 calculation corresponds to the case of $c = 0$. The present procedure for determining the core potential integral is a practical method for considering the shielding effect upon the core Coulomb repulsion and is particularly useful when we use smaller γ_{AB}'s estimated semi-empirically [11–13] than those obtained by Pople and Segal [10].

Configuration Analysis Method. The ground state wave functions of inter- and intra-molecular hydrogen-bonding systems calculated by the modified CNDO/2 method mentioned above, were analysed by the configuration analysis method presented by Baba, Suzuki, and Takemura [21]. As the reference wave functions in these analyses, the ground and singly excited configurations constructed from the monomer MO's were adopted for the intermolecular dimers, and the ground configuration and the singly and doubly excited configurations constructed from the MO's of the maleate dinegative ion and from the 1s orbital of the hydrogen-bonded hydrogen, were adopted for the hydrogen maleate ion.

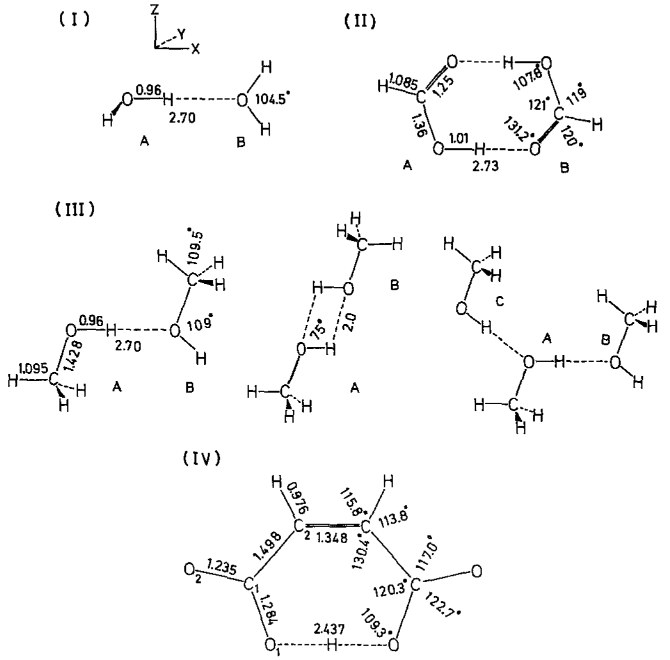

Fig. 1. The geometrical structures of the hydrogen-bonded systems: (*I*) the water dimer, (*II*) the formic acid dimer, (*III*) the methanol dimers and trimer, and (*IV*) the hydrogen maleate ion

Molecular Parameters. The geometries and the molecular parameters of hydrogen-bonded water, methanol, formic acid and hydrogen maelate ion are shown in Fig. 1. These molecular parameters were taken from the electron [22, 23] and X-ray [24, 25] diffraction studies and also from other works [7, 26]. In the water dimer, the left hand side (A-site) molecule lies in the $x-y$ plane, while the other (B-site) molecule in the $x-z$ plane. The molecular geometries of the cyclic dimers were assumed to have the C_{2h} symmetry, and for the cyclic dimer of methanol, the O···H distance and the H–O···H angle were taken to be 2.0 Å and 75°, respectively, by referring to the results calculated by the CNDO/2 method [3, 4].

3. Results and Discussion

The total energies of the water and formic acid monomers and the water dimer were calculated by the modified CNDO/2 method, the c (in Eq. (2)) value and the O–H, C=O, or O···O interatomic distance being changed. The values of c in the core potential integrals, V_{AB}^c, were determined to be $c_{OH}=0.21$, $c_{CO}=0.38$, and $c_{OO}=0.77$ for the O–H, C=O, and O···O, respectively, in such a way as the calculated bond lengths are coincident with the observed ones [27–30] as well as possible: the γ_{AB}^c values calculated by the use of the above c values are shown in Fig. 2, together with the values of the two-center Coulomb integrals, γ_{AB}, obtained by Eq. (1).

The total energies of the monomer and dimer of water calculated with the above-mentioned c values are -383.91 and -768.20 eV, respectively, and the monomer and dimer of formic acid are -871.54 and -1744.57 eV, respectively. According to the present calculation, hydrogen bonding energies are obtained to be 0.38 and 1.49 eV for water and formic acid, respectively.

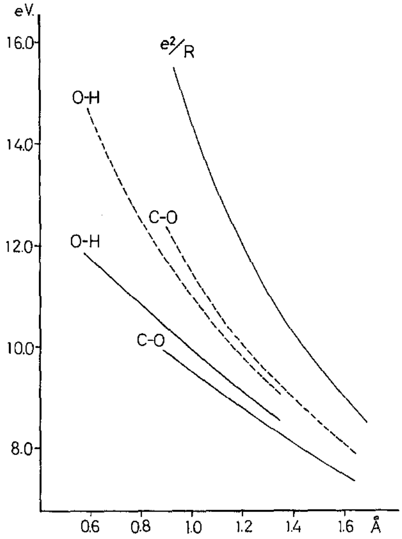

Fig. 2. The core potential integrals (γ_{AB}^c) and the two center Coulomb integrals (γ_{AB}) for O–H and C=O bonds. ——— γ_{AB}, - - - - - γ_{AB}^c

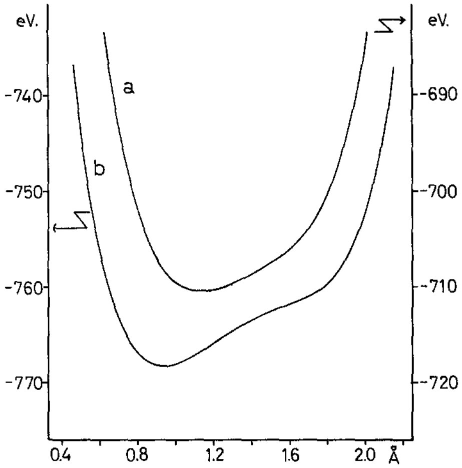

Fig. 3. The total energy (eV) calculated for the water dimer as a function of the hydrogen-bonded O–H distance (Å), the O···O distance being fixed at 2.70 Å. The c values in Eq. (2) are taken as follows: $c_{OH}=c_{OO}=0$ for (a); $c_{OH}=0.21$ and $c_{OO}=0.77$ for (b)

Potential Energy Curves for Hydrogen-Bonded Systems. The potential energy curve for the water dimer was calculated by the modified CNDO/2 method; the result is shown in Fig. 3. The shape of the potential energy curve calculated for the linear dimer of methanol is entirely the same as that of the water dimer. The potential energy curve (b) calculated with $c_{OH}=0.21$ and $c_{OO}=0.77$ has a minimum at r(O–H) = 0.95 Å and a concavity near 1.70 Å and is qualitatively in good agreement with the curve calculated by Murthy, Davis, and Rao for methanol [3]. The value of r(O–H) calculated with the c values is in better agreement with the observed value [31] than the value calculated with $c=0$ (r(O–H) = 1.12 Å). From curve (b), the fundamental frequency, ν_{OH}, was obtained to be $\sim 5900\,\text{cm}^{-1}$[1]; this is 1.8 times larger than the observed frequency [16]. Our result for the methanol or water dimer shows a concavity in addition to the potential minimum. Experimentally, a double minimum potential energy curve was obtained for the linear chain hydrogen bond of formic acid in pure liquid from the analysis of the overtone bands [8]. From an analogy with this case, the linear dimer of methanol or water may be expected to show a double minimum potential energy curve.

Potential energy curves calculated for the formic acid dimer are shown in Fig. 4. The solid lines in this figure indicate the total energy calculated by varing the two hydrogen-bonded O–H distances simultaneously from 0.7 ~ 1.3 Å on the assumption that the other atoms are fixed on the experimentally determined molecular geometry [23] and by using the core potential integrals with $c_{OH}=0.21$, $c_{CO}=0.38$, and $c_{OO}=0.77$. The broken line in Fig. 4 indicates the total energy calculated for the system with the four equivalent C–O bonds of 1.27 Å [30].

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[1] This frequency was calculated by the aid of the analytical potential curve, $v(q)=\frac{1}{2}[15q+4q^2+100q^3+128q^4]$, which was determined to coincide with the potential energy curve (b) in Fig. 3 as well as possible.

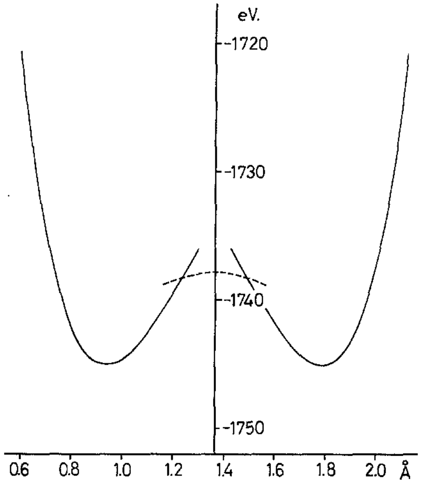

Fig. 4

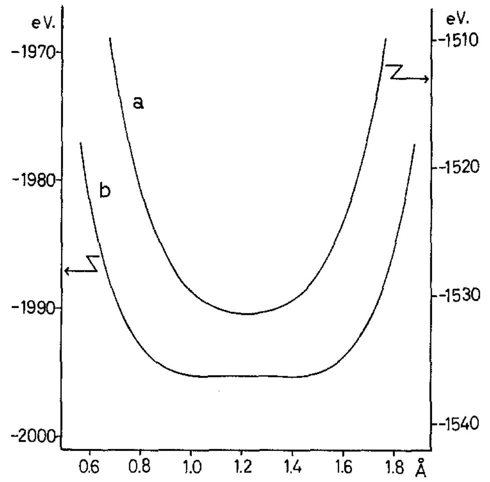

Fig. 5

Fig. 4. The total energy (eV) calculated for the coupled O–H stretching vibration of the formic acid dimer, the O···O distance being fixed at 2.73 Å

Fig. 5. The total energy (eV) calculated for the hydrogen maleate ion as a function of the hydrogen-bonded O–H distance (Å), the O···O distance being fixed at 2.437 Å. The c values in Eq. (2) are taken as follows: $c_{OH} = c_{CO} = c_{OO} = 0$ for (*a*); $c_{OH} = 0.21$, $c_{CO} = 0.38$, and $c_{OO} = 0.77$ for (*b*)

The potential energy curve in Fig. 4 gives the equilibrium O–H bond length of 0.95 Å and the barrier height of 7.3 eV. The calculated bond length agrees well with the spectroscopically determined one (1.01 Å) [26], but the calculated barrier height and the calculated fundamental frequency ($\sim$15100 cm^{-1})[2] are too large compared to the experimentally determined values (0.80 $\sim$ 0.86 eV, $\sim$3110 cm^{-1}) [8, 32]. This discrepancy may be due to a little lower ($\sim$0.16 eV) estimation of the γ_{AB}^{c} value for the O–H bond at comparatively large distances ($\sim$ 1.365 Å). According to the total energy calculated for the formic acid dimer at r(O–H) = 1.365 Å by the use of the γ_{AB}^{c} values of $c = 0.29$ (which is 0.16 eV larger than the one of $c = 0.21$) the barrier height is reduced to 0.8 eV. This value is nearly equal to the experimentally determined one [8]. This fact suggests that better theoretical potential energy curves can be obtained by taking into account the O–H bond length dependency of c.

Now let us turn to the hydrogen maleate ion. The potential energy curve calculated for this ion is shown in Fig. 5. Curve (b) calculated with $c_{OH} = 0.21$, $c_{CO} = 0.38$, and $c_{OO} = 0.77$ shows a flat-bottomed symmetrical potential energy curve with a negligibly small barrier. This coincides well with the expectation from the experimental point of view for this strong hydrogen bond [33]. The calculated fundamental frequency for curve (b) is about 1660 cm^{-1}[3], in good agreement with the observed one [33].

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[2] This frequency was calculated by the aid of the analytical potential curve, $v(q) = \frac{1}{2} \times 193q^2 + 48.0 \exp(-4.0q^2)$, with the barrier height of 7.3 eV and with the energy minimum at r(O–H) = 0.95 Å, which was simulated for the potential energy curve of Fig. 4.

[3] This frequency was calculated by the aid of the analytical potential curve, $v(q) = \frac{1}{2}[q^2 + 180q^4]$, which was determined in such a way to fit as well as possible into curve (*b*) in Fig. 5.

Configuration Analyses for Hydrogen-Bonded Systems. The results of the configuration analyses obtained for the linear dimers of water and methanol and for the cyclic dimers of methanol and formic acid are given in Tables 1–3. In these tables, G denotes the ground configuration, and $i-j$ represents a singly excited configuration of the monomer in which one electron on the i-th occupied orbital is excited to the j-th vacant orbital. In the present calculation, the monomer MO's were calculated by the modified CNDO/2 method for each monomer component of the dimer, and the orbitals are numbered in such a way that MO's belonging to the A- and B-components are denoted by odd and even numbers in the order of increasing orbital energies, respectively. Singly excited configurations in which i and j are both even numbers or both odd numbers correspond to locally-excited configurations, while those in which i is even and j is odd or vice versa, correspond to intermolecular charge-transfer configurations.

The configuration analyses were performed by taking all the singly excited configurations. For the cyclic methanol and formic acid dimers, owing to their C_{2h} symmetry, the singly excited configurations having the indices of $2m-2n$

Table 1. The result of the configuration analysis obtained for the ground state of the water dimer at $R(O\cdots O)=2.50$, 2.70, and 2.90 Å

Group	Configuration	Weights		
		2.50 Å	2.70 Å	2.90 Å
A	G	0.9271	0.9596 (0.9632)[a]	0.9788
B	6–9	0.0267	0.0151	0.0079
	6–11	0.0313	0.0176	0.0092
	2–9	0.0022	0.0012	0.0006
	2–11	0.0029	0.0015	0.0008
	Total for group B	0.0631	0.0354 (0.0352)	0.0185
C	5–12	0.0002	0.0001	0.0001
	3–12	0.0007	0.0004	0.0002
	1–12	0.0004	0.0002	0.0001
	Total for group C	0.0013	0.0007 (0.0007)	0.0004
$D(A)$	5–11	0.0007	0.0003	0.0002
	3–9	0.0016	0.0008	0.0004
	1–11	0.0005	0.0002	0.0001
	Total for group $D(A)$	0.0028	0.0013 (0.0003)	0.0007
$D(B)$	6–12	0.0005	0.0004	0.0003
	4–10	0.0027	0.0017	0.0010
	2–12	0.0007	0.0004	0.0003
	Total for group $D(B)$	0.0039	0.0025 (0.0005)	0.0016
Total		0.9982	0.9995 (0.9998)	1.0000

[a] The values in the parentheses are calculated by taking all the c values to be zero.

Table 2. The result of the configuration analysis obtained for the ground states of the linear and cyclic dimers of methanol

Group	Configuration	Weights	
		Linear dimer	Cyclic dimer
A	*G*	0.9576	0.9747
		(0.9639)[a]	(0.9826)[a]
B	12–23	0.0181	0.0036
	10–23	0.0052	0.0023
	6–23	0.0059	0.0001
	4–23	–	0.0006
	2–23	0.0026	0.0006
	Total for	0.0318	0.0072
	group *B*	(0.0296)	(0.0073)
B'	12–21	0.0007	0.0003
	10–21	0.0001	0.0001
	6–21	0.0002	0.0003
	4–21	–	0.0003
	2–21	0.0001	0.0001
	Total for	0.0011	0.0011
	group *B'*	(0.0029)	(0.0009)
B''	12–17	0.0011	0.0003
	10–17	0.0003	0.0001
	6–17	0.0003	–
	2–17	0.0001	–
	Total for	0.0018	0.0004
	group *B''*	(0.0023)	(0.0005)
C	11–24	0.0002	
	9–24	0.0001	
	5–24	0.0002	
	3–24	0.0002	
	1–24	0.0002	
	Total for	0.0009	
	group *C*	(0.0008)	
D(*A*)	11–23	0.0001	0.0002
	5–23	0.0001	0.0001
	3–23	0.0001	0.0002
	1–23	0.0001	0.0002
	Total for	0.0004	0.0007
	group *D*(*A*)	(0.0007)	(0.00005)
D(*B*)	12–24	0.0012	
	etc.		
D'(*A*)	9–21	0.0002	0.0006
	5–21	0.0001	0.0004
	3–21	–	0.0001
	Total for	0.0003	0.0011
	group *D'*(*A*)		
D'(*B*)	10–22	0.0009	
	etc.		
D''(*A*)	1–21	–	0.0002

[a] The values in the parentheses are calculated, by taking all the *c* values to be zero.

Table 2 (continued)

Group	Configuration	Weights	
		Linear dimer	Cyclic dimer
$E(A)$	13–19	0.0006	0.0013
	11–17	0.0003	0.0004
	9–15	0.0001	0.0001
	9–17	0.0001	–
	5–15	–	0.0001
	Total for group $E(A)$	0.0011	0.0019
$E(B)$	14–20 etc.	0.0026	
$E'(B)$	12–16	0.0001	
Total		0.9998 (1.0002)	0.9999[b] (1.0001)[b]

[b] The other counterpart of each configuration (B, B', B'', D, D', D'', and E) is involved.

are equivalent to those of $(2m-1)-(2n-1)$, and $2m-(2n-1)$ to $(2m-1)-2n$, where m and n are integers. For these cyclic dimers only one of the equivalent two configurations is listed in Tables 2 and 3.

By considering the characteristics of the monomer MO's and the signs of the expansion coefficients, configurations belonging to Group (A), (B), ..., and (F) can be classified into the two types of configurations; namely, the intermolecular charge-transfer and locally-excited configurations as shown in Fig. 6.

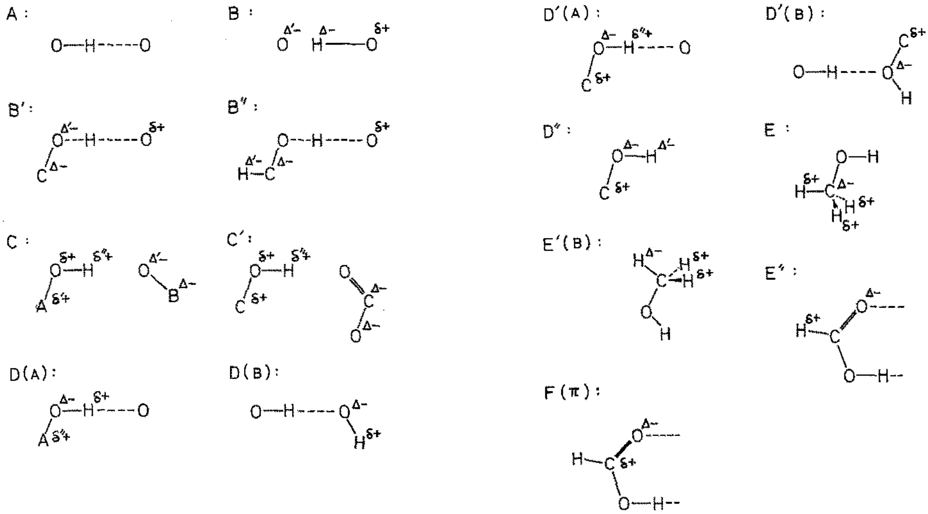

Fig. 6. Configurations of Groups (A), (B), ..., and (F). In configuration (C), B atom represents the hydrogen atom for the water and methanol dimers, and the carbon atom for the formic acid dimer. $\sigma \gtrsim \sigma' \gg \sigma''$ and $\Delta \gtrsim \Delta' \gg \Delta''$ generally hold

Table 3. The result of the configuration analysis obtained for the ground state of the formic acid dimer

(*A*) The contribution of each configuration to the ground state at R(O···O) = 2.73 Å

Group	Configuration	Weight	Group	Configuration	Weight
A	*G*	0.9014	*D*	13–27	0.0003
B	15–26	0.0014		5–27	0.0001
	15–28	0.0050		1–27	0.0001
	9–26	0.0005	*D′*	7–25	0.0002
	9–28	0.0023		5–25	0.0002
	3–26	0.0003	*E*	15–23	0.0001
	3–28	0.0013		7–21	0.0003
B″	15–24	0.0005		5–23	0.0001
	9–24	0.0006		5–21	0.0001
	9–22	0.0001	*E″*	15–21	0.0007
	3–24	0.0002		13–21	0.0003
C	13–22	0.0002	*F*	17–19(π)	0.0215
	7–24	0.0004		11–19(π)	0.0064
	7–22	0.0001			
	5–22	0.0001			
	1–22	0.0001			
C′	13–26	0.0004			
	13–28	0.0010			
	7–26	0.0001			
	7–28	0.0009			
	5–26	0.0003			
	5–28	0.0005			
	1–26	0.0001			
	1–28	0.0004			

(*B*) The contribution of each group to the ground state at *R*(O···O) = 2.53, 2.73, and 2.93 Å

Group	Weights		
	2.53 Å	2.73 Å	2.93 Å
A	0.8338	0.9014	0.9413
B	0.0190	0.0108	0.0058
B″	0.0026	0.0014	0.0007
C	0.0019	0.0009	0.0005
C′	0.0063	0.0037	0.0020
D	0.0010	0.0005	0.0003
D′	0.0006	0.0004	0.0002
E	0.0008	0.0006	0.0005
E″	0.0011	0.0010	0.0007
F(π)	0.0437	0.0279	0.0182
Total[a]	0.9880	0.9960	0.9991

[a] The other counterpart of each configuration (*B*, *B″*, ..., and *F*) is involved.

As is clearly seen in Tables 1 and 2, the natures of hydrogen bonds are similar to each other for the linear dimers of water and methanol[4], except for the fact that the latter has a small contribution of configuration (*E*) which comes from

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[4] The same result was obtained for the neighboring two component molecules of the linear trimer of methanol.

the polarization of the methyl group. For these linear dimers, the intermolecular charge-transfer configuration (*B*) contributes significantly to the ground state. The contributions of configurations (*B*′), (*B*″), (*C*), (*D*(*B*)), (*D*′), and (*E*) show that the effect of hydrogen-bonding can not be simply expressed by the effect within the fictitious three atom model, O–H···O. This conclusion is consistent with that of Morokuma and Pedersen [7]. According to the present calculation the water dimer has only a negligibly small contribution of the $O^+H^-\cdots O$ configuration although a valence bond treatment [34] predicted a fairly large contribution of the configuration.

As is clearly seen in Table 2, the contributions of the configurations (*B*) and (*B*″) are much smaller for the cyclic dimer of methanol than for the linear dimer[5]. These facts suggest that the former is mainly stabilized by the electrostatic interaction and is less stabilized by the delocalization energy (charge-transfer energy) than the latter.

Because of the delocalization of the monomer MO's, the nature of the formic acid dimer is a little complicated. As is seen in Table 3, beside the configuration (*B*), the configurations (*B*″), (*C*′), (*E*″), and (*F*)[6] contribute to the ground state of the formic acid dimer. Of these, configuration (*F*) is a locally-excited π-electron configuration.

For the water and formic acid dimers, the configuration analyses were performed taking various O···O distances; the results are tabulated in Tables 1 and 3. When the O···O distances are shortened by 0.2 Å, the contributions of the excited configurations increase about two times.

The core potential integrals used in our modified CNDO/2 calculations are different from those used by other authors [3–5, 9–13]. We made also the calculation taking $c=0$ for all bonds. The obtained wave functions were analysed by the configuration analysis method. The results of the configuration analysis listed in Tables 1 and 2 are found to be rather insensitive to the choice of the core potential integrals.

Now let us turn to the hydrogen maleate ion. The configuration analysis was performed, the MO's of the maleate dinegative ion calculated by the modified CNDO/2 method and the 1*s* orbital[7] of the hydrogen-bonded hydrogen being employed as reference orbitals; the result is tabulated in Table 4. The configurations of groups (*A*), (*B*), ..., and (*F*) are shown in Fig. 7. In order to obtain the satisfactory convergence for this case, it is necessary to take doubly excited configurations in addition to singly excited ones. The doubly excited configurations of the $V_{ik,ik}$ and $V_{ik,jk}$ types (i and j represent occupied MO's, and k, vacant MO's) significantly contribute mainly to the configurations (*F*) and (*A*), respectively. The doubly excited configurations of the $V_{ik,jl}$ type (i and j represent σ and π occupied MO's, respectively, and k and l, σ and π vacant MO's, respectively) contribute to the configuration, (*A*)+(*C*′), and the doubly excited configuration

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[5] Owing to the C_{2h} symmetry of the cyclic dimer, configuration (*C*) is equivalent to configuration (*B*).

[6] More strictly, each of the (*D*), (*E*), (*E*″), and (*F*) groups for the formic acid dimer can be divided into two or more subgroups.

[7] This orbital is treated as a vacant orbital in the present analysis.

Table 4. The result of the configuration analysis obtained for the ground state of the hydrogen maleate ion

Group	Weights	
	Singly excited configurations	Doubly excited configurations
A	0.3558	0.0827[a]
$A+C'$ (or C)		0.0002[b] 0.0942[c]
$A+E''$		0.0002[b] 0.0064[c]
B	0.2945	
C	0.0019	
C'	0.0771	0.0007[b] 0.0052[c] 0.0019[d]
D	0.0001	
D'	0.0003	
E	0.0004	
E'	0.0004	
E''	0.0053	
$C'+E''$		0.0012[c]
F		0.0246[d]
Total	0.9531	

[a] From doubly excited configurations, $V_{ik,jk}$.
[b] From doubly excited configurations, $V_{ik,il}$.
[c] From doubly excited configurations, $V_{ik,jl}$.
[d] From doubly excited configurations, $V_{ik,ik}$.

of the $V_{ik,jl}$ type ($i \neq j$, $k \neq l$, and all indeces represent σ MO's), to the $(A)+(E'')$ configuration.

Table 4 shows that configurations corresponding to the covalent structure of hydrogen bond (namely, singly excited configuration (A) and doubly excited configurations (A), $(A)+(C')$ and $(A)+(E'')$), contributes to the ground state of the hydrogen maleate ion by 54%, while the contribution of configurations corresponding to the ionic structure (namely, singly excited configurations (B), (C), (C'), (E), (E'), (E'') and doubly excited configuration (C')) is 39%. It is worth noticing that the covalent character is more predominant for the hydrogen bond of the hydrogen maleate ion than the ionic character.

Charge Shift due to Hydrogen-Bond Formation. The charge shift due to hydrogen-bond formation of water, methanol, formic acid, and hydrogen maleate ion are shown in Fig. 8. For the linear dimers of water and methanol, the hydrogen-bond formation causes the electron migration from the hydrogen atom and the methyl group of B-component molecule to the proton accepting oxygen atom, and further from both the proton accepting oxygen atom and the hydrogen-bonded hydrogen atom to the proton-donating oxygen atom. The electron migration corresponds to the large contribution of configurations (B) and (D) to the ground state of the dimers. This result is in agreement with that obtained by others [3, 4]. The calculated dipole moments of the monomer and

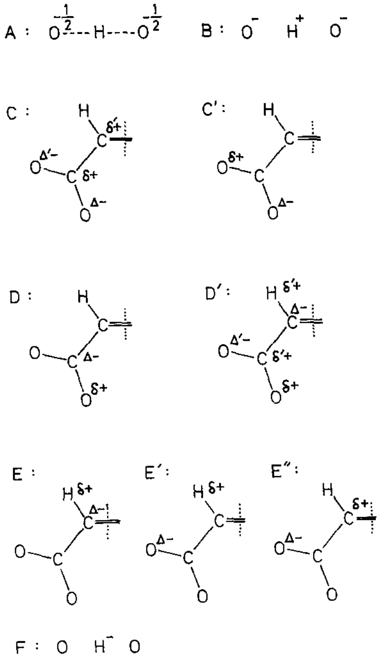

Fig. 7. Configurations of Groups (*A*), (*B*), ..., and (*F*) for the hydrogen maleate ion

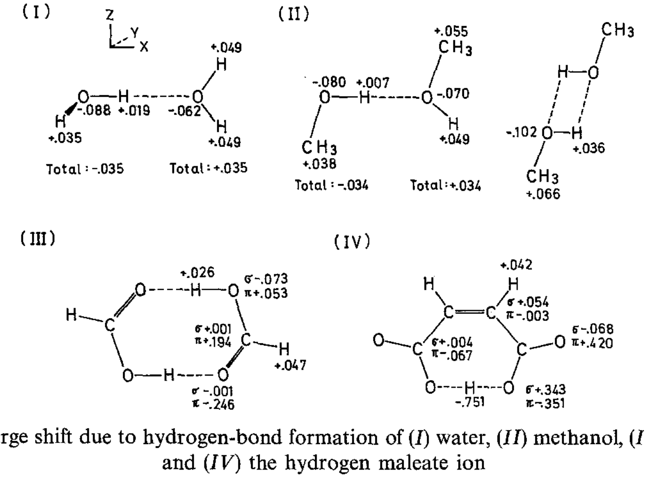

Fig. 8. The charge shift due to hydrogen-bond formation of (*I*) water, (*II*) methanol, (*III*) formic acid, and (*IV*) the hydrogen maleate ion

the linear dimer of water are 1.73 (exp. 1.82 [35]) and 3.70 *D*, respectively, and those of methanol are 1.51 (exp. 1.71 [35]) and 3.20 *D*, respectively. Compared to the linear dimers, O–H bonds are more polarized in the cyclic dimer of methanol in hydrogen-bond formation.

For the hydrogen-bonded formic acid, σ electrons move from the hydrogen-bonded hydrogen atom to the oxygen atom (–O–), while π electrons move from the oxygen atom (–O–) and the carbon atom to the oxygen atom (=O). Therefore, the excess σ electrons on the oxygen atom (–O–) are compensated by π electrons. The dipole moment of monomeric formic acid was calculated to be 0.65 (exp. 1.7 [35]) *D*.

In hydrogen-bond formation (i.e., when the proton is attached to the maleate dinegative ion), σ electron density on the hydrogen-bonded oxygen atom, O_1 decreases greatly, while π electrons move from the oxygen atom, O_2 to O_1.

The calculated dipole moment of the hydrogen maleate ion is 1.94 *D*.

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Prof. Dr. S. Nagakura, The Institute for Solid State Physics, The University of Tokyo
Roppongi, Minato, Tokyo, Japan